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AROMATIC DEODORIZING COMPOSITION FOR EXCREMENT

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Abstract

Problem

A perfume component that is not decomposable by digestive enzymes but by enterobacteria is separated and formed, and a fragrance desirable to people is rendered to excrement with said perfume component to mask the malodor. Even when it is used in

combination with a conventional deodorizing agent, the disappearance of fragrance due to said agent does not occur, but instead the deodorizing effect is synergistically improved.

#### Solving means

This is a fragrant deodorizing composition for excrement containing a compound obtained by converting a perfume compound into a perfume glycoside having  $\beta$  bonding as an effective component. It is preferable that the perfume compound have a hydroxyl group and that the blended concentration of the perfume glycoside with respect to said composition be in the range of about 0.01 to about 30 wt%.

#### Claims

1. A fragrant deodorizing composition for excrement characterized by the fact that a perfume glycoside having  $\beta$  bonding for the bonding of a perfume compound and a saccharide is contained as an effective component.
2. A fragrant deodorizing composition for excrement characterized by the fact that a perfume glycoside having  $\beta$  bonding for the bonding of a perfume compound having a hydroxyl group and a saccharide is contained as an effective component.
3. The fragrant deodorizing composition for excrement described in Claim 1 or 2, characterized by the fact that the blended concentration of the perfume glycoside with respect to said composition is in the range of about 0.01 to about 30 wt%.

#### Detailed explanation of the invention

[0001]

##### Technical field of the invention

The present invention relates to a fragrant deodorizing composition for excrement.

[0002]

##### Prior art

In order to deodorize the odor of excrement of humans, pets, domestic animals and so on, numerous fragrance agents for releasing fragrance by placing or spreading them in toilets or indoors to mask malodor and deodorizing agents for eliminating the odor of excrement through oral intake have already been provided. As deodorizing agents of the oral intake type, biscuits blended with silica gel (Japanese Kokai Patent Application No. Hei 6[1994]-339344), a mushroom extract for neutralization of or addition reaction with malodorous substances (Japanese Kokai Patent Application No. Hei 5[1993]-38358), solely food fibers for improving enterobacteriaceae plexus and decreasing the formation of decayed metabolic products with

malodor (Japanese Kokai Patent Application No. Hei 6[1994]-217761), a combination of food fibers and tannic acid (Japanese Kokai Patent Application No. Hei 6[1994]-256180) and so on are available.

[0003]

Problems to be solved by the invention

Since the odor of excrement is mainly a composite odor of multiple components like ammonia, mercaptans, amines, indole, skatole and so on, as metabolic products due to enterobacteria, it is difficult to cope with all of the malodorous components of excrement with the previously mentioned deodorizing agents of the oral intake type. The deodorization of excrement has been incomplete. Furthermore, even if a perfume is taken orally in an attempt to render a fragrance to excrement in order to mask the malodor, it is absorbed and metabolized when it reaches the digestive tract. Since the fragrance is lost, the fragrance cannot be rendered to excrement.

[0004]

Means to solve the problems

The present inventors have zealously conducted research in order to solve such problems. On the basis of a discovery that an anticipated effectiveness could be rendered by freeing a perfume component decomposed by enterobacteria but not decomposed by digestive enzymes and discharging this perfume component together with the excrement, it has been found that enterobacteria producing ammonia, mercaptans, amines, indole, skatole and so on, as causes of the unpleasant odor of excrement can efficiently decompose a perfume glycoside having  $\beta$  bonding to free a perfume component and to generate a fragrance. The present invention has thus been accomplished. In regard to this, the present inventors have first clarified that this has not previously been reported.

[0005]

In other words, the present invention relates to a fragrant deodorizing composition for excrement containing a compound obtained by converting a perfume compound into a perfume glycoside having  $\beta$  bonding as the effective component. It is preferable from viewpoints of favored characteristics and fragrant deodorizing effect if the blended concentration of the perfume glycoside with respect to the fragrant deodorizing composition for excrement is in the range of about 0.01 to about 30 wt%, although it varies with the threshold value of the perfume component constituting the perfume glycoside and cannot be specified uniquely. It is preferable that the perfume component have a hydroxyl group. Furthermore, as perfume glycosides, all

those having  $\beta$  bonding that is not readily decomposed by digestive enzymes but is decomposed by enterobacteria to free perfume components can be used.

[0006]

Specifically, as aglycones equivalent to perfume compounds, cis-3-hexenol, linalool, geraniol, nerol, citronellol, rosinol [transliteration], dimethyloctanol, hydroxy citronellol, tetrahydrolinalool, lavandulol, myrcenol,  $\alpha$ -terpineol, 1-menthol, borneol, dimethylphenylcarbinol,  $\beta$ -phenylethyldimethylcarbinol,  $\beta$ -phenylethylmethylethylcarbinol, phenoxyethyl alcohol, phenyl glycol, tertiary butyl cyclohexanol, hydroxy citronellal, methyl salicylate, ethyl salicylate, isopropyl salicylate, isoamyl salicylate, benzyl salicylate, phenylethyl salicylate, linalool oxide, vanillin, ethyl vanillin, lilal [transliteration], maltol, thymol, carvacrol, eugenol, isoeugenol, isopulegol, nopol, farnesol, nerolidol, santalol [transliteration], cedrol, vetiverol, benzyl alcohol, 2-phenylethyl alcohol,  $\gamma$ -phenylpropyl alcohol, cinnamic alcohol, anisic alcohol, dimethylbenzylcarbinol, methylphenylcarbinol and so on can be mentioned.

[0007]

As the saccharide portion, monosaccharides (glucose, galactose, mannose, glucosamine, galactosamine, rhamnose, xylose, ribose, arabinose, and so on), and disaccharides (sucrose, lactose, maltose, gentiobiose, cellobiose, isomaltose, primeverose, bisianose [transliteration], rutinose, and so on) can be mentioned.

[0008]

The bonding of a perfume compound and a saccharide is a  $\beta$  bonding that is not readily decomposed by digestive enzymes but is decomposed by enterobacteria. As perfume glycosides, commercial ones are readily available, but they can also be synthesized by publicly known methods. Extracts containing perfume glycosides can be obtained from natural raw materials.

[0009]

The fragrant deodorizing composition for excrement of the present invention can be manufactured by blending more than one perfume glycoside mentioned previously. A variety of compositions generating fragrance based on perfume compounds equivalent to the aglycone portion are included. Specifically, cold beverages, confectioneries, frozen desserts, dairy products, wines, meats, deodorized foods and other foods, raw bacterial agents, medicines for the stomach and bowels, pet foods, domestic animal feeds and so on, can be mentioned.

[0010]

Next, synthesis examples of perfume glycosides and the results of decomposition tests by enzymes will be given.

[0011]

#### Synthesis of geranyl- $\beta$ -D-glucoside

According to the method disclosed in Yu Kagaku Vol. 43, pages 31-38 (1994), 2.39 g geraniol and 4.11 g tetraacetyl- $\alpha$ -D-glucose bromide were dissolved in ether; 7.1 g silica gel-supported silver carbonate and 5 g molecular sieve 4A were added; and a reaction was conducted at 40°C. After distilling off the ether, the reaction product was hydrolyzed with sodium methoxide. Furthermore, after neutralization with a cation-exchange resin, the reaction product was purified by silica gel column chromatography to obtain 1.49 g geranyl- $\beta$ -D-glucoside (yield 47%).

[0012]

The nuclear magnetic resonance spectrum of geranyl- $\beta$ -D-glucoside ( $\text{CD}_3\text{OD}$ )  $\delta$  (ppm):

1. 60  
(3 H, s), 1. 68 (6 H, s), 2. 08 (4  
H, m), 3. 17 (4 H, m), 3. 63~3. 89  
(2 H, dd), 4. 20~4. 37 (2 H, m),  
4. 28 (1 H, d,  $J = 7.7 \text{ Hz}$ ), 5. 10 (1  
H, t), 5. 36 (1 H, t)

[0013]

#### Synthesis of 2-phenylethyl- $\beta$ -D-glucoside

With a partial modification in the maltol saccharide derivative synthesis method disclosed in Yu Kagaku Vol. 44, pages 23-29 (1995), 20.0 g 2-phenylethyl alcohol and 14.0 g cellobiose were dissolved in 1 L of McIlvaine buffer solution (pH 4.5), and 10.0 g Cellular Zeamano [transliteration] T were added to cause a reaction. This reaction solution was purified by chromatography using XAD-2 gel by methanol elution to obtain 1.21 g 2-phenylethyl- $\beta$ -D-glucoside (yield 7%).

[0014]

#### Synthesis of cis-3-hexenyl- $\beta$ -D-glucoside

According to the method disclosed in Yu Kagaku Vol. 43, pages 31-38 (1994), 1.58 g cis-3-hexenol and 4.11 g tetraacetyl- $\alpha$ -D-glucose bromide were dissolved in ether; 7.1 g silica gel-supported silver carbonate and 5 g molecular sieve 4A were added; and a reaction was

conducted at 40°C. After distilling off the ether, the reaction product was hydrolyzed with sodium methoxide. Furthermore, after neutralization with a cation-exchange resin, the reaction product was purified by silica gel column chromatography to obtain 1.05 g cis-3-hexenyl- $\beta$ -D-glucoside (yield 40%).

[0015]

#### Synthesis of linalool oxide- $\beta$ -D-glucoside

According to the method disclosed in Yu Kagaku Vol. 43, pages 31-38 (1994), 2.64 g linalool oxide and 4.11 g tetraacetyl- $\alpha$ -D-glucose bromide were dissolved in ether; 7.1 g silica gel-supported silver carbonate and 5 g molecular sieve 4A were added; and a reaction was conducted at 40°C. After distilling off the ether, the reaction product was hydrolyzed with sodium methoxide. Furthermore, after neutralization with a cation-exchange resin, the reaction product was purified by silica gel column chromatography to obtain 0.51 g linalool oxide- $\beta$ -D-glucoside (yield 15%).

[0016]

#### Test on decomposition with amyloglucosidase

In order to investigate whether a perfume glycoside was a substrate for amyloglucosidase as a digestive enzyme, a test was conducted on the decomposition of a perfume glycoside with amyloglucosidase. The products were evaluated by TLC. For geranyl- $\beta$ -D-glucoside, 2-phenylethyl- $\beta$ -D-glucoside, and cis-3-hexenyl- $\beta$ -D-glucoside, 200  $\mu$ L of 10 mg/mL McIlvaine buffer liquid solution (pH 4.5) were prepared, and 200  $\mu$ L of amyloglucosidase 0.56 mg/mL McIlvaine buffer liquid solution (pH 4.5) were added. This was allowed to stand at 55°C. After 6 h, products were confirmed by TLC. The test results are shown in Table 1.

[0017]

#### Test on decomposition with lipase

In order to investigate whether a perfume glycoside was a substrate for lipase as a digestive enzyme, a test was conducted on the decomposition of a perfume glycoside with lipase. The products were evaluated by TLC. For geranyl- $\beta$ -D-glucoside, 2-phenylethyl- $\beta$ -D-glucoside, and cis-3-hexenyl- $\beta$ -D-glucoside, 200  $\mu$ L of 10 mg/mL sodium phosphate buffer liquid solution (pH 7.7) were prepared, and 200  $\mu$ L of lipase 21.4  $\mu$ g/mL buffer sodium phosphate liquid solution (pH 7.7) were added. This was allowed to stand at 37°C. After 6 h, products were evaluated by TLC. The test results are shown in Table 1.

[0018]

Test on decomposition with  $\beta$ -glucosidase

In order to investigate whether a perfume glycoside was a substrate for  $\beta$ -glucosidase [possessed by] enterobacteria, a test was conducted on the decomposition of a perfume glycoside with  $\beta$ -glucosidase. The products were evaluated by TLC. At the same time, the formation of a perfume component from the perfume glycoside was evaluated by using gas chromatography. For geranyl- $\beta$ -D-glucoside, 2-phenylethyl- $\beta$ -D-glucoside, and cis-3-hexenyl- $\beta$ -D-glucoside, 5 mL of 10 mg/mL citric acid buffer liquid solution (pH 5.0) were prepared, and 50 mg  $\beta$ -glucosidase were added. This was allowed to stand at 37°C. After 1 h, TLC analysis was conducted. Furthermore, the perfume component was extracted with ether and analyzed with gas chromatography. The test results are shown in Tables 1 and 2.

[0019]

Table 1

	アミログルコ シダーゼ ①	リパーゼ ②	$\beta$ -グルコシ ダーゼ ③
④ ゲラニル- $\beta$ -D- グルコシド	-	-	+
⑤ 2-フェニルエチル- $\beta$ -D-グルコシド	-	-	+
⑥ シス-3-ヘキセニル - $\beta$ -D-グルコシド	-	-	+

-: The substrate remained without decomposition. +: The substrate was virtually decomposed.

Key: 1 Amyloglucosidase  
 2 Lipase  
 3  $\beta$ -Glucosidase  
 4 Geranyl- $\beta$ -D-glucoside  
 5 2-Phenylethyl- $\beta$ -D-glucoside  
 6 Cis-3-hexenyl- $\beta$ -D-glucoside

[0020]

Table 2 ③

	香料配糖体 ①	生成香料成分 ②	生成量 (mg) ③	分解率 (%) ④
⑤	ゲラニル-β-D-グルコシド	ゲラニオール ⑥	4.78	98
⑦	2-フェニルエチル-β-D-グルコシド	2-フェニルエチルアルコール ⑧	4.28	99.7
⑨	シス-3-ヘキセニル-β-D-グルコシド	シス-3-ヘキセノール ⑩	3.52	92.1

Key: 1 Perfume glycoside  
 2 Perfume component formed  
 3 Amount formed (mg)  
 4 Percentage decomposed (%)  
 5 Geranyl-β-D-glucoside  
 6 Geraniol  
 7 2-Phenylethyl-β-D-glucoside  
 8 2-Phenylethyl alcohol  
 9 Cis-3-hexenyl-β-D-glucoside  
 10 Cis-3-hexenol

[0021]

As shown in Table 1, the perfume glycoside was not decomposed with amyloglucosidase and lipase as digestive enzymes. However, it was decomposed rapidly with β-glucosidase possessed by enterobacteria. Furthermore, as shown in Table 2, perfume components were formed from perfume glycosides with β-glucosidase.

[0022]

Test on perfume glycoside metabolism with enterobacteria

Tests concerning perfume glycoside metabolism with enterobacteria were conducted, and the formation of perfume components from the perfume glycosides was evaluated using gas chromatography. To 5 mL of PYF (Peptone Yeast extract Fildes solution) culture, 10 mM of 2-phenylethyl-β-D-glucoside were added. In this liquid culture, a 0.4% bacterial solution of a variety of enterobacteria cultivated in EGF (Eggerth Gagnon Fildes solution) culture was inoculated. Anaerobic cultivation was conducted at 37°C. After cultivation for two days, the product was extracted with ether and analyzed by gas chromatography. The results are shown in Table 3.



[0023]

Table 3 ③

①	菌 株	生成香料成分 ②	生成量 (mg)	分解率 (%) ④
	<i>Clostridium perfringens</i>	2-フェニルエチル アルコール ⑤	5. 6 1	9 2
	<i>Lactobacillus acidophilus</i>	2-フェニルエチル アルコール ⑤	2. 8 1	4 3
	<i>Lactobacillus casei</i>	2-フェニルエチル アルコール ⑤	5. 4 7	9 0
	<i>Bacteroides fragilis</i>	2-フェニルエチル アルコール ⑤	0	0
	<i>Bifidobacterium adolescentis</i>	2-フェニルエチル アルコール ⑤	4. 4 9	7 4
	<i>Peptostreptococcus productus</i>	2-フェニルエチル アルコール ⑤	1. 2 2	2 0

Key: 1 Strain  
 2 Perfume component formed  
 3 Amount formed (mg)  
 4 Percentage decomposed (%)  
 5 2-Phenylethyl alcohol

[0024]

As shown in Table 3, five out of the six strains of enterobacteria tested formed 2-phenylethyl alcohol from the perfume glycoside.

[0025]

Implementation embodiments of the invention

The present invention will be further explained in detail by giving application examples in the following. However, the scope of the present invention is not to be restricted to these application examples.

[0026]

#### Application Examples 1 through 3 and Comparative Example

Candies were prepared from the recipes shown in Table 4. These candies were prepared according to an ordinary manufacturing method.

[0027]

Table 4

	①	①	①	②
	実施例 1	実施例 2	実施例 3	比較例
③ グラニュー糖	50部	50部	50部	50部
⑤ 水飴 (D. E. 42)	50部	50部	50部	50部
⑥ 水	20部	20部	20部	20部
⑦ 香料	1部	1部	1部	1部
⑧ ゲラニル- $\beta$ -D-グルコシド	2部	-	-	-
⑨ 2-フェニルエチル- $\beta$ -D-グルコシド	-	2部	-	-
⑩ シス-3-ヘキセニル- $\beta$ -D-グルコシド	-		2部	-

- Key: 1 Application Example \_\_  
 2 Comparative Example \_\_  
 3 Granular sugar  
 4 \_\_ part(s)  
 5 Millet jelly (D. E. 42)  
 6 Water  
 7 Perfume  
 8 Geranyl- $\beta$ -D-glucoside  
 9 2-Phenylethyl- $\beta$ -D-glucoside  
 10 Cis-3-hexenyl- $\beta$ -D-glucoside

[0028]

## Sensory evaluation test

For a fragrant deodorizing composition for excrement of the present invention, in order to evaluate its fragrant deodorizing effect and flavor, a sensory test was conducted with a panel consisting of 20 persons (25-56 years old) consisting of 10 adult men and 10 adult women. In an eating period of three days (6 g per day) per week by the panel, they were allowed to eat compositions of Application Examples 1 through 3 and the comparative example (for a total of 4 weeks). At the same time, in regard to the flavor and the odor of excrement, judgments were made according to the evaluation criteria shown in Table 5. The fragrant deodorizing effect with respect to flavor and the excrement odor was evaluated by scores. The results are shown in Table 6.

[0029]

Table 5

A 芳香消臭作用	B 臭 気 強 度	C 快・不快度
(H) 2 → (J) 3 →	0 無臭 (D)	+2 快 (E)
	1 やっと感知できるにおい (F)	+1 やや快 (G)
	2 何のにおいであるかわかる 弱いにおい	0 快でも不快でもない (I)
	3 楽に感知できるにおい	-1 やや不快 (K)
	4 強いにおい (L)	-2 不快 (M)
	5 強烈なにおい (N)	
O 風 味	+2 おいしかった (P) +1 ややおいしかった (Q) 0 ふつう (R) -1 おいしくなかった (S)	

- Key:
- A Fragrant deodorizing effect
  - B Odor strength
  - C Comfort or discomfort
  - D 0 Odorless
  - E +2 Comfort
  - F 1 Odor sensed barely
  - G +1 Some comfort
  - H 2 Some odor detected but weak
  - I 0 Neither comfort nor discomfort
  - J 3 Odor sensed easily
  - K -1 Some discomfort
  - L 4 Strong odor
  - M -2 Discomfort
  - N 5 Intense odor
  - O Flavor
  - P +2 Delicious
  - Q +1 Somewhat delicious
  - R 0 Fair
  - S -1 Not delicious

[0030]

Table 6

	① 風 味	② 芳 香 消 臭 作 用			⑤
		臭気強度③	認容性 ④	便に芳香を感じた人	
⑥ 比較例	0.15	4.6	-1.9	2	
⑦ 実施例 1	0.20	3.2	-0.5	14	
⑦ 実施例 2	0.15	4.0	-1.5	5	
⑦ 実施例 3	0.15	3.0	-0.3	16	

Key: 1 Flavor  
 2 Fragrant deodorizing effect  
 3 Odor strength  
 4 Detectable  
 5 Persons sensing fragrance in excrement  
 6 Comparative Example \_\_  
 7 Application Example \_\_

[0031]

As shown in Table 6, in regard to the flavor, evaluations in Application Examples 1 through 3 were virtually unchanged in comparison with the comparative example. However, it was confirmed that fragrance in excrement was detected in Application Examples 1 through 3. Furthermore, a deodorizing effect was found.

[0032]

#### Application Example 4

A candy was prepared according to the recipe shown in the following.

Granular sugar	45 parts
Millet jelly (D. E. 42)	50 parts
Water	20 parts
Green tea extract (deodorizing agent)	3 parts
Linalool oxide- $\beta$ -D-glucoside	3 parts
Perfume	1 part

[0033]

Application Example 5

A chewing gum was prepared according to the recipe shown in the following using the ordinary method customarily employed.

A gum base	20 parts
Sugar	56 parts
Millet jelly	13 parts
Glucose	10 parts
Cis-3-hexenyl- $\beta$ -D-glucoside	5 parts
Softening agent	1 part
Perfume	0.5 part

[0034]

Application Example 6

A chewing gum was prepared according to the recipe shown in the following.

A gum base	20 parts
Sugar	56 parts
Millet jelly	13 parts
Glucose	10 parts
2-Phenylethyl- $\beta$ -D-glucoside	5 parts
Green tea extract (deodorizing agent)	1 part
Softening agent	1 part
Perfume	0.5 part

[0035]

Application Example 7

A chocolate was prepared according to the recipe shown in the following using the ordinary method customarily employed.

Cacao bitar [transliteration]	20 parts
Cacao butter	17 parts
Sugar	43 parts
Powdered whole milk	20 parts
Geranyl- $\beta$ -D-glucoside	1 part
Perfume	0.2 part

[0036]

Application Example 8

A tablet agent was prepared according to the recipe shown in the following by using the ordinary method customarily employed.

Lactose	100 parts
Potato starch	100 parts
2-Phenylethyl- $\beta$ -D-glucoside	60 parts

[0037]

Application Example 9

Biscuits were prepared according to the recipe shown in the following by using the ordinary method customarily employed.

Soft flour	100 parts
Shortening	30 parts
Powdered sugar	32 parts
Millet jelly (D. E. 42)	5 parts
Powdered skim milk	1.8 parts
Table salt	1.1 parts
Commercial 2-phenylethyl- $\beta$ -D-galactoside (manufactured by Sigma Co.)	1 part
A swelling agent	0.45 part

[0038]

## Effect of the invention

The perfume glycoside of the present invention, in the case of oral intake, is not readily decomposed with digestive enzymes contained in saliva. However, by decomposition with enterobacteria, a perfume component is separated and formed, and this is discharged together with excrement during a bowel movement. Such a perfume component renders a floral fragrance, green note and other aromas favored by people. Furthermore, it has been found that the malodor of excrement is masked and neutralized.

[0039]

According to the composition of the present invention, since the perfume component is present as a perfume glycoside, even if it is used in combination with a conventional deodorizing agent, disappearance of the fragrance due to the conventional deodorizing agent does not occur.

Instead, it has been observed that the deodorizing effect is additive or even synergistically increased.